Short communication

Self-protective cobalt nanocatalyst for long-time recycle application on hydrogen generation by its free metal-ion conversion

Zhi-Li Wang, Jun-Min Yan*, Hong-Li Wang, Qing Jiang*

Key Laboratory of Automobile Materials, Ministry of Education, and Department of Materials Science and Engineering, Jilin University, Changchun 130022, China

HIGHLIGHTS

- We have explored a facile but very efficient method to realize the long-time recycle application of Co nanocatalyst.
- Oxidizes Co^0 completely into Co^{2+} for the long-time and oxygen-fearless storage in air.
- Reduces Co^{2+} back to fresh and highly active Co^0 for the recycle application in air.
- There is no obvious decrease in activity after 20th recycle application (73 days) for hydrogen generation in air.

ABSTRACT

Cobalt nanoparticles have attracted much attention in nanocatalysis due to their low cost and high activities. However, the easy-oxidative deactivation of cobalt nanocatalysts in air seriously limits their practical applications, especially in a long-time recycle application. Herein, by intentionally taking advantage of the readily oxidizable character of metallic cobalt, we describe a simple but efficient method to overcome the above obstacle through a free and reverse metal-ion conversion of cobalt in air at room temperature. With this novel method, the cobalt nanocatalyst demonstrates the superior activity even after the long-time (73 days) recycle application for hydrogen generation from ammonia borane.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Nanocatalysis contributes significantly to many important chemical reactions due to the large surface-to-volume ratio and the enhanced catalytic activity of the nanocatalyst compared to its bulk counterpart [1–3]. A key objective of nanocatalysis is to produce catalyst with 100% selectivity, extremely high activity, low cost, and especially long-time stability [4,5]. Cobalt (Co), as a much more abundant element in the earth's crust than noble metals, has been intensively studied because of its relatively low cost and very potent catalytic properties in many important reactions [6–9]. However, compared to the noble-metal catalysts, Co nanoparticles (NPs) are much more easier to be oxidized in air, and thus leads to the deactivation and poor recycle stability especially when a long

interval between two recycle applications is needed, which seriously limits their practical applications [10,11]. Current methods to overcome this problem are focused on coating Co NPs with some robust outer shells, such as silica, carbon, transition-metal oxides and so on [12–15], or applying and storing the catalysts under inert atmosphere [16]. However, these methods suffer from more or less drawbacks like modestly catalytic activity (due to the occupation of active sites by coating materials), complicated and uneconomical process for catalyst preparation and application [12–16]. Thereafter, exploring new strategies to effectively avoid the deactivation of Co NPs is highly desirable but still a big challenge.

With greenhouse gas emissions affecting environmental climates, the need for alternative fuels has become abundantly clear. Hydrogen has emerged as secure, renewable, inexhaustible, emission-free fuel [17]. However, finding efficient and safe hydrogen storage materials remains one of the most difficult challenges on the way to the fuel cell based hydrogen economy [18–20]. Ammonia borane (NH_3BH_3, AB) has been considered as a

---

* Corresponding authors.
  E-mail addresses: junminyan@jlu.edu.cn, jiangq@jlu.edu.cn (J.-M. Yan).

potential hydrogen storage material because of its high hydrogen content (19.6 wt%), high solubility and stability at room temperature and nontoxicity [21–25]. Recently, Co NPs have attracted an increasing level of attentions as catalysts for hydrogen generation from hydrolysis of AB owing to their high activities and low cost [26–28]. Although Co NPs are not easily to be oxidized under a reductive atmosphere of AB aqueous solution during the reaction, the big hurdle for their practical application also lies on their easy oxidative deactivation if for the recycle application with a long-time interval in water and air [29].

Ideally, when nanocatalysts are recycling applied, their activities are well maintained as high as those of the fresh catalysts. Therefore, refreshing the nanocatalysts may be a promising solution to recover the high activities of catalysts in recycles applications. Herein, by intentionally taking advantage of the readily oxidizable character of Co NPs in air, we describe a simple but efficient method to overcome the above obstacle of Co NPs. The concept lies on the facile, free, as well as reverse conversion between Co^0 NPs and Co^{2+} cations. Namely, oxidizes Co^0 completely into Co^{2+} for the long-time and oxygen-fearless storage, and reduces Co^{2+} back to fresh and highly active Co^0 for the recycle application. In the overall experiments, $NaBH_4$ is used as the reducing agent. To the best of our knowledge, the present metal-ion conversion is a novel way to successfully prevent the deactivation of nanocatalysts.

2. Experimental methods

2.1. Chemicals

Ammonia borane (AB, Aldrich, 90%), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, Beijing Chemicals Works, >99%), ammonium chloride (NH_4Cl, Beijing Chemicals Works, >99%), sodium borohydride ($NaBH_4$, Sinopharm Chemical Reagent Co., Ltd, >96%), and ammonia solution (NH_4OH, Beijing Chemicals Works, 25%–28%) are used without further purification.

2.2. Characterization

Transmission electron microscope (TEM) (Tecnai F20, Philips) was applied for the detailed microstructure and composition information. The TEM samples were prepared by depositing one or two droplets of the NPs suspended in aqueous solution onto the amorphous carbon coated copper steel grids, which were then dried in argon (Ar) atmosphere. Ultraviolet and visible (UV–Vis) absorption spectra were recorded on an Agilent Cary 50 spectrophotometer in the wavelength range of 350–750 nm. Powder X-ray diffraction (XRD) patterns were performed on a Rigaku RINT-2000 X-ray diffractometer with Cu Kα. X-ray photoelectron spectrometry (XPS) analyses were carried out on an ESCALABMKLL X-ray photoelectron spectrometer using an Al Kα source.

2.3. Synthesis and reverse metal-ion conversion of Co system

Typically, 50 mg of AB and 10 mg of $NaBH_4$ was dissolved in 5 mL of distilled water, then $CoCl_2$ aqueous solution (0.006 M, 5 mL) was added into the above solution with magnetic stirring, and the black Co NPs were rapidly generated.

After the reaction, the black suspension (pH = 9.4) was magnetic stirred in air to oxidative etch the Co NPs. After 30 min of etching, the black suspension was changed into the pink solution. Then, the same amount of reducing agent as the initial experiment ($NaBH_4$ 10 mg, AB 50 mg) was readded into the pink solution to get the black Co NPs again. Such mental-ion conversion can be repeated freely for at least 20 times. All the reactions were performed at room temperature (293 K).

The above metal-ion conversion was traced by UV–Vis spectra. The initial-generated Co NPs was analyzed by XPS, and the reaction solution without Co NPs was used for UV–Vis analysis. To investigate the stability of the reformed pink solution, the solution was stored in air for two months, and then UV–Vis was performed on this solution again.
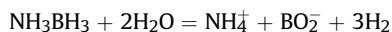
To find the impact factors on the metal-ion conversion, the following three experiments were applied: (1) Etching the Co NPs under Ar atmosphere. $CoCl_2$ (0.006 M, 5 mL) was purged with Ar for 1 h, and then 5 mL of aqueous solution containing the mixture of the $NaBH_4$ (10 mg) and AB (50 mg) was added into the above solution in Ar with 200 min. (2) Etching the pure Co NPs dispersed in distilled water in air. After the initial generation of Co NPs, they were separated from the reaction solution and washed by distilled water for several times, and then 10 mL distilled water was added into the pure Co NPs. Finally, the black suspension without ions was magnetic stirred in air for 200 min. (3) Etching the pure Co NPs dispersed in ammonia solution in air. After the initial generated of Co NPs, they were separated and washed, and then, 10 mL of distilled water was added into the pure Co NPs. The pH value of the black suspension was changed to 9.4 (as the initial reaction solution) by adding ammonia solution. Finally, the above suspension was magnetic was magnetic stirred in air for 200 min.

2.4. Heat treatment of the initial-generated Co NPs

After the initial-generated Co NPs were separated from the reaction solution and dried in Ar atmosphere, they were transferred into a furnace where a continuous Ar gas flow was introduced. Then, the furnace temperature was elevated to 873 K and maintained for 3 h. The as-obtained Co sample after heart treatment was used for XRD analysis.

2.5. Catalytic activity and recycle application of Co NPs

5 mL of aqueous solution containing $NaBH_4$ (10 mg) and AB (50 mg) was kept in a two-necked round-bottom flask. One neck was connected to a gas burette, and the other was connected to a pressure-equalization funnel to introduce $CoCl_2$ aqueous solution (0.006 M, 5 mL). The hydrogen generation reaction was begun once the $CoCl_2$ solution was added into the round-bottom flask containing AB and $NaBH_4$ solution with magnetic stirring. The evolution of gas was monitored using the gas burette. The hydrolysis of AB can be briefly expressed as follow:

$$NH_3BH_3 + 2H_2O = NH_4^+ + BO_2^- + 3H_2$$

After the hydrolysis reaction catalyzed by the *in situ* prepared Co NPs was completed, the reaction solution was stirred in air to etch the Co NPs. 30 min later, the clear pink solution containing regenerated Co^{2+} actions was obtained, and this pink solution was then stored in air for 7 days. After the long-time storage in air, the same amount of $NaBH_4$ and AB as the first time was readded into the pink solution to regenerate the Co NPs, and the recycle activity of the regenerated Co NPs to AB hydrolysis was tested again.

The above recycle tests were performed for 10 times (63 days). The initial-generated and the 10th regenerated Co NPs were used for TEM and XRD analyses. To save the experimental time and further characterize the recycle stability of Co NPs, another 10 times (10 days) of recycle tests with every interval of 1 day were continued to apply on the above 10th regenerated Co NPs in air at 293 K.

For comparison, the initial-generated Co NPs were washed and stored in 10 mL of distilled water for 7 days to mostly avoid the oxidative etching of Co NPs. After 7 days, AB (50 mg) was added into

the above solution and hydrogen generation from this system was monitored using the gas burette. In addition, the continuous recycle stability of the initial-generated Co NPs was also studied as follows: after the catalytic hydrolysis of AB was completed, another equivalent of AB (50 mg) was added to the reaction system again without interval, and the released gas was monitored by the gas burette. Such recycle experiments for the synthesized catalyst were repeated for 5 times.

3. Results and discussion

3.1. Metal-ion conversion of Co NPs

The experimental progress is schematically illustrated in Fig. 1, and visibly monitored by the evolution of the solution color in Fig. 2 inset. Typically, $CoCl_2$ aqueous solution, as the precursor of Co NPs, shows its characteristic color in pink (Fig. 2, inset a). Once a certain amount of the reducing agent of $NaBH_4$ with the presence of AB is added, the color suddenly changes to black (Fig. 2, inset b). The XPS result of the black specimen reveals that it is in the state of metallic Co, and no boride has been found (Fig. 3) [30], indicating the formation of Co NPs. After the dehydrogenation of AB catalyzed by the formed Co NPs, the black suspension is magnetic stirred in air. The suspension changes its black color gradually back to pink within 30 min (Fig. 2, inset c), which implies that Co NPs may be returned to Co^{2+} cations. To confirm this assumption, UV–Vis absorption spectroscopy is employed to monitor the above conversion (Fig. 2). It is obvious that a broad absorption peak at ~510 nm (Fig. 2a), corresponding to $CoCl_2$, disappears after addition of reducing agent, implying the rapid reduction of Co^{2+} to Co NPs (Fig. 2b). After the black suspension changes back to clear pink solution, the peak at ~510 nm appears again (Fig. 2c). It should be noted that the strong absorption below 420 nm is attributed to the reaction products (NH_4^+ and BO_2^-) of this system (Figs. S1 and S2). Based on the above results, it is certain that the as-prepared Co NPs can be easily converted into Co^{2+} cations by simply stirring the solution in air for only 30 min. Moreover, the reformed Co^{2+} cations are very stable and unchanged even after two months' storage in air (Fig. S3).

To detailedly find the impact factors on this free conversion between Co^0 and Co^{2+} in the reaction system in air, the black suspension of Co NPs is stirred for 200 min in Ar atmosphere. As a result, the black Co NPs suspension is stable in Ar (Fig. S4a). Therefore, oxygen, as the only reactive gas in air to Co NPs at room temperature, is one of the key factors resulting in the free metal-ion conversion, and thus the conversion process of Co^0 NPs to Co^{2+} is the oxidative etching process. Additionally, with the absence of any ions, the washed Co NPs in distilled water can not be changed into Co^{2+} even after stirring for 200 min in air, which is deduced by its black color (Fig. S4b). Moreover, NH_4^+ cations in this system are fund have no impact on the metal-ion conversion (Fig. S4c). Therefore, Cl^- and BO_2^- anions in the reaction solution also play an important role on the above metal-ion conversion. It is reported that surface

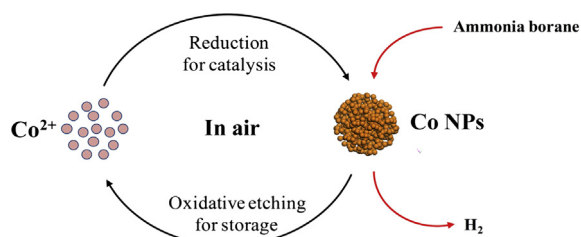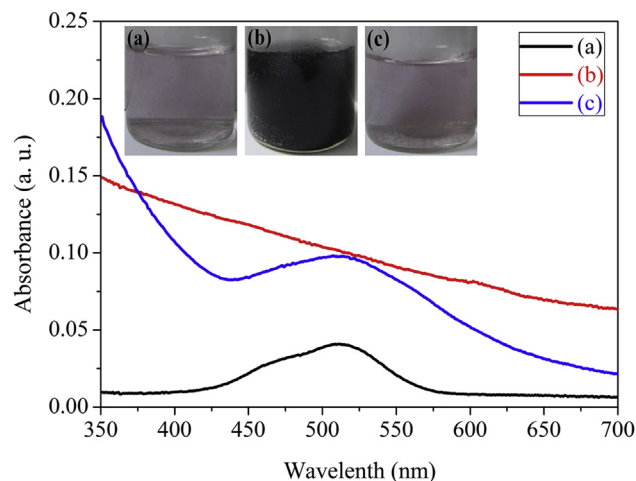**Fig. 2.** UV–Vis spectra of (a) $CoCl_2$ solution, (b) Co NPs and (c) the solution after oxidative etching of Co NPs in air. The inset shows the corresponding color for (a) $CoCl_2$ solution, (b) Co NPs, (c) the solution after oxidative etching of Co NPs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

atoms on noble metal nanocrystals, such as Ag and Pd, could be partly etched by O_2/Cl^- pair [31,32]. Thus, the present oxidative etching is likely caused by the combining effect of oxygen from air and anions from the reaction system. Although the above phenomenon that Co NPs can be oxidative etched to Co^{2+} in the present solution in air is not a very novel discovery, until now, there is no report on long-time recycle application of Co nanocatalyst by taking its priority of easy oxidative etching in air.

After etching, the reformed Co^{2+} cations can be easily reduced back to black Co NPs by the same amount of $NaBH_4$, and this reverse conversion between Co^0 and Co^{2+} can be further repeated freely in air. Thereby, the free and reverse metal-ion conversion has the priority to be applied on recycle application of Co NPs in catalysis, in which, after catalytic reaction, Co NPs can be transformed into Co^{2+} and stored easily and safely in air; while when the catalytic reaction is high activity even after long-time opening to air, which is much needed to be performed again, Co^{2+} can be then conveniently reduced back to Co NPs as active catalyst without deactivation even after a long-time storage in aqueous solution in air.

3.2. Catalytic activity and recycle application of Co NPs

Taking advantage of the free metal-ion conversion, the long-time recycle application of Co catalyst is investigated in air at 293 K. Fig. 4 shows the volume of H_2 generated as a function of reaction time at different recycle numbers. It can be seen that, with the initial-generated Co NPs, the catalytic hydrolysis of AB can be completed within 11 min, and the generated H_2 gas from the system has a volume of 125 mL (Fig. 4a). After reaction, the Co NPs are oxidative etched and stored in air for 7 days, and then they are reduced back to Co NPs and applied for the same catalytic reaction again. Such recycle test is repeated for 10 times. As a result, the regenerated Co NPs also exhibit the same excellent activity as the initial Co NPs (Fig. 4b). Moreover, continuing the recycle test for another 10 times with every interval of 1 day to save the experimental time, there is still no obvious decrease in activity for the regenerated Co NPs (Fig. S5), suggesting that the regenerated Co NPs are retained its high activity even after 73 days. For comparison, washing and storing the initial-generated Co NPs in pure water in air for 7 days, and then applying them on the same catalytic reaction (without re-addition of $NaBH_4$), unfortunately, the
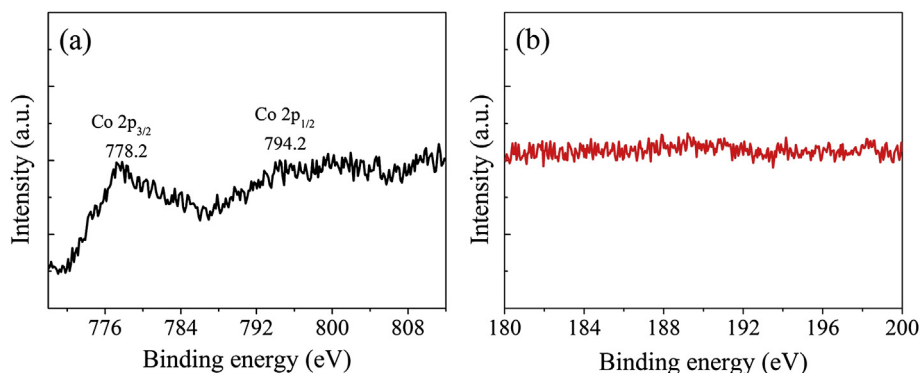

Fig. 1. Illustration for the recyclable preparation, catalytic application and oxidative etching of Co NPs.

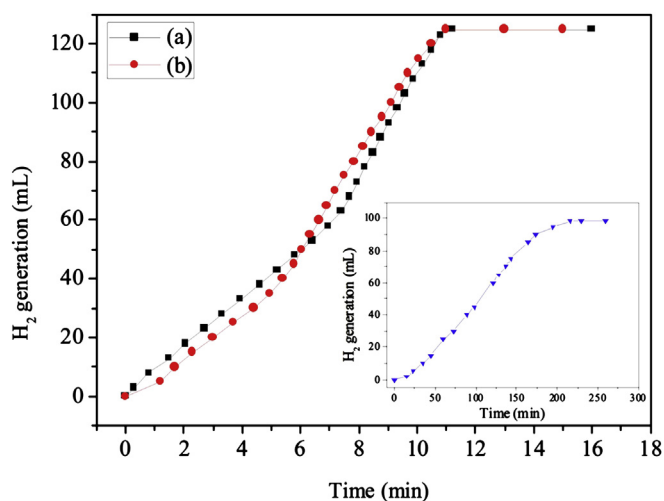**Fig. 3.** XPS results for elements of (a) Co and (b) B of the initial-generated Co NPs.

Fig. 4. Hydrogen generation from AB (0.29 M, 5 mL) catalyzed by (a) the initial-generated Co NPs, and (b) the 10th regenerated at 293 K. Inset: hydrogen generation from AB catalyzed by the washed Co NPs storing in pure water in air for 7 days (Co/AB = 0.02).

reaction can be completed only after a long period of 216 min (Fig. 4 inset). In addition, storing the initial-generated Co NPs in air for 7 days and applying for the same reaction with re-addition of AB and NaBH₄, the reaction can be completed during 38 min (Fig. S6). Moreover, the continuous recycle stability of the initial-generated Co NPs is also studied. The result shows that the reaction time is prolonged to be 30 min after the 5th recycle test (Fig. S7). Based on the above results, it is proved that the metal-ion conversion can be used as a new method to overcome the oxidative deactivation of

the Co NPs and maintain their initial-beneficial for the commercial application of Co nanocatalysts.

3.3. Discussion

Fig. 5 shows the TEM images of the initial-generated and the 10th regenerated Co NPs with every interval of 7 days. It is found that the initial-generated Co NPs with average sizes of ∼20 nm are aggregated and in a nanochain-like structure (Fig. 5a). The corresponding SAED (Fig. 5a inset) and XRD studies (Fig. 6a) reveal that the specimen is in amorphous state. After heat treatment at 873 K for 3 h in Ar, the amorphous phase is crystallized into face-centered-cubic Co (Fig. 6c, JCPDS: 15-0806) [33], which further indicates the formation of Co NPs. The TEM image of the 10th regenerated Co NPs shows well dispersion with a much smaller average particle size of ∼4 nm (Fig. 5b). The corresponding SAED (Fig. 5b inset) and XRD (Fig. 6b) also reveal the amorphous state of Co NPs. It has been reported that amine containing material (atearylamine) could act as the dispersion agent for synthesis of Co–Fe/Cr NPs [34]. In this sense, the obtained well dispersing Co NPs, which is greatly different from their initial aggregation state, may be attributed to the increased amount of ammonium (NH₄⁺) in the reaction system from AB hydrolysis. Thus, the present strategy has also provided an efficient way toward the easy synthesis of well dispersed Co NPs. However, the smaller and well dispersed Co NPs do not lead to the final enhancement of the catalytic activity in the present system (Fig. 4). It can be understand that, during the 10th *in situ* re-generation of Co NPs, the reduction process of Co^{2+} by NaBH₄ has been prolonged due to the increasing pH value of the reaction system after continuous addition of AB and NaBH₄ [35]. Thus, in the first 6 min, the initial-generated Co NPs lead to the higher reaction rate compared to the 10th regenerated one. Once Co NPs with smaller particle sizes are completely reformed, they show
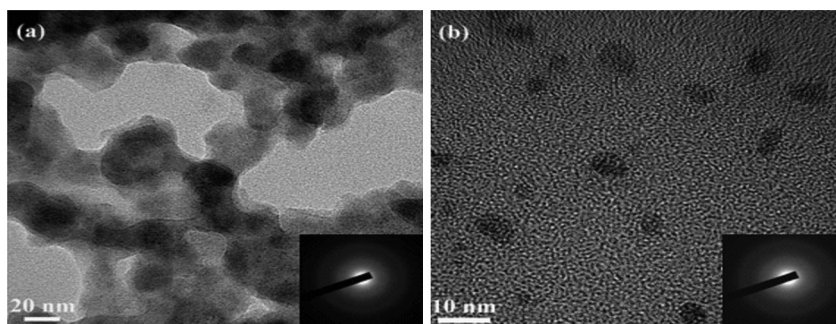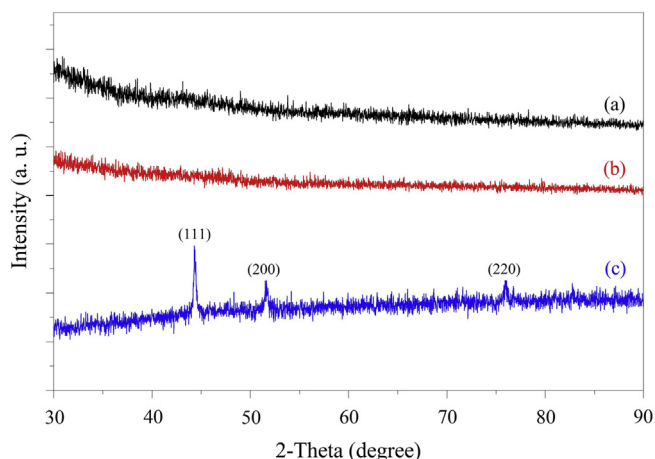

Fig. 5. TEM images and corresponding SAED patterns of (a) the initial-generated Co NPs and (b) the 10th regenerated Co NPs.

Fig. 6. XRD patterns of (a) the initial-generated Co NPs, (b) the 10th regenerated Co NPs, and (c) the initial-generated Co NPs after heart treatment at 873 K in Ar for 3 h.

the higher reaction rate than that of the initial-generated one in the next 5 min (Fig. 4). Moreover, it is found that ammonium (NH_4^+) species in the reaction solution has a little suppressing effect on the catalytic activity of Co NPs (Fig. S8). Consequently, the initial-generated and the 10th regenerated Co NPs finally demonstrate the same catalytic activities for the whole reaction.

4. Conclusion

We have explored a facile, low-cost, but very efficient metal-ion conversion method to overcome the deactivation of Co nanocatalyst during the long-time recycle application in air. The regenerated Co NPs maintain their initial-high activity for AB hydrolysis. Such metal-ion conversion process may represent a new strategy to overcome the oxidative deactivation for non-noble catalysts for future development on the practical on-board hydrogen storage/supply material.

Acknowledgments

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2013.05.193.

References

[1] N. Tian, Z.Y. Zhou, S.G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732—735.
[2] B. Lim, M. Jiang, P.H.C. Camargo, E.C. Cho, J. Tao, X. Lu, Y. Zhu, Y. Xia, Science 324 (2009) 1302—1305.
[3] M.K. Carpenter, T.E. Moylan, R.S. Kukreja, M.H. Atwan, M.M.T. Tessema, J. Am. Chem. Soc. 134 (2012) 8535—8542.
[4] K. Tedsree, T. Li, S. Jones, C.W.A. Chan, K.M.K. Yu, P.A.J. Bagot, E.A. Marquis, G.D.W. Smith, S.C.E. Tsang, Nat. Nanotechnol. 6 (2011) 302—307.
[5] S. Guo, S. Sun, J. Am. Chem. Soc. 134 (2012) 2492—2495.
[6] K. Takeuchi, T. Matsuzaki, T.A. Hanaoka, H. Arakawa, Y. Sugi, K. Wei, J. Mol. Catal. 55 (1989) 361—370.
[7] L. Brossard, B. Marquis, Int. J. Hydrogen Energy 19 (1994) 231—237.
[8] J. Ahmed, S. Sharma, K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, J. Colloid Interface Sci. 336 (2009) 814—819.
[9] W. Liu, Y.F. Zhu, Q. Jiang, J. Phys. Chem. C 114 (2010) 21094—21099.
[10] R.N. Grass, E.K. Athanassiou, W.J. Stark, Angew. Chem. Int. Ed. 46 (2007) 4909—4912.
[11] D.L. Huber, Small 1 (2005) 482—501.
[12] V.F. Puntes, K.M. Krishnan, A.P. Alivisatos, Science 291 (2001) 2115—2117.
[13] T. Sen, A. Sebastianelli, I.J. Bruce, J. Am. Chem. Soc. 128 (2006) 7130—7131.
[14] Ö. Metin, S. Özkar, S. Sun, Nano Res. 3 (2010) 676—684.
[15] Y. Yamada, K. Yano, S. Fukuzumi, Energy Environ. Sci. 5 (2012) 5356—5363.
[16] Ö. Metin, V. Mazumder, S. Özkar, S. Sun, J. Am. Chem. Soc. 132 (2010) 1468—1469.
[17] P. Chen, Z.T. Xiong, J.Z. Luo, J.Y. Lin, K.L. Tan, Nature 420 (2002) 302—304.
[18] H.L. Jiang, S.K. Singh, J.M. Yan, X.B. Zhang, Q. Xu, ChemSusChem 3 (2010) 541—549.
[19] Z.W. Zhang, J.C. Li, Q. Jiang, J. Phys. Chem. C 114 (2010) 7733—7737.
[20] A.D. Sutton, A.K. Burrell, D.A. Dixon, E.B. Garner, J.C. Gordon, T. Nakagawa, K.C. Ott, J.P. Robinson, M. Vasiliu, Science 331 (2011) 1426—1429.
[21] M. Chandra, Q. Xu, J. Power Sources 156 (2006) 190—194.
[22] J.M. Yan, X.B. Zhang, S. Han, H. Shioyama, Q. Xu, Angew. Chem. Int. Ed. 47 (2008) 2287—2289.
[23] S.K. Kim, W.S. Han, T.J. Kim, T.Y. Kim, S.W. Nam, M. Mitoraj, L. Piekos, A. Michalak, S.J. Hwang, S.O. Kang, J. Am. Chem. Soc. 132 (2010) 9954—9955.
[24] P.Z. Li, K. Aranishi, Q. Xu, Chem. Commun. 48 (2012) 3173—3175.
[25] M. Yadav, Q. Xu, Energy Environ. Sci. 5 (2012) 9698—9725.
[26] J.M. Yan, X.B. Zhang, H. Shioyama, Q. Xu, J. Power Sources 195 (2010) 1091—1094.
[27] J.M. Yan, X.B. Zhang, T. Akita, M. Haruta, Q. Xu, J. Am. Chem. Soc. 132 (2010) 5326—5327.
[28] Q. Xu, M. Chandra, J. Power Sources 163 (2006) 364—370.
[29] F.H. Stephens, R.T. Baker, M.H. Matus, D.J. Grant, D.A. Dixon, Angew. Chem. Int. Ed. 46 (2007) 746—749.
[30] http://www.lasurface.com/database/elementxps.php.
[31] B. Lim, M. Jiang, J. Tao, P.H.C. Camargo, Y. Zhu, Y. Xia, Adv. Funt. Mater. 19 (2009) 189—200.
[32] C.L. Lu, K.S. Prasad, H.L. Wu, J.A. Ho, M.H. Huang, J. Am. Chem. Soc. 132 (2010) 14546—14553.
[33] D. Wang, Y. Li, J. Am. Chem. Soc. 132 (2010) 6280—6281.
[34] M. Yamada, M. Arai, M. Kurihara, M. Sakamoto, M. Miyake, J. Am. Chem. Soc. 126 (2004) 9482—9483.
[35] H. Lee, S.E. Habas, S. Kweskin, D. Butcher, G.A. Somorjai, P. Yang, Angew. Chem. Int. Ed. 118 (2006) 7988—7992.